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PREPARATION OF POLYMERS USING METAL-CARBENES. (U)

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Preparations of Polymers Using Metal-Carbenes

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Thomas J. Katz, Steven J. Lee, and Michael A. Shippey

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Preparations of Polymers Using Metal-Carbenes

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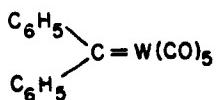
Summary

Metal-carbenes initiate the polymerizations of cycloalkenes to polyalkenamers that are stereoselectively cis, cyclic trisubstituted olefins to polymers that are translationally invariant, and acetylenes to polyacetylenes. Some implications are described.

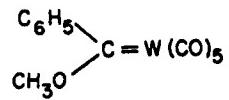
The recent analyses of the mechanism of the olefin metathesis reaction [1] suggest new ways to make polymers and new polymers to make.

They suggest, for example, that appropriate metal-carbenes should initiate metatheses, and in a number of experiments commonly available metal-carbenes have indeed proven effective. We summarize here some of these experiments, which also evidence two kinds of stereoselectivity, one for a favored geometrical isomer and one for a favored direction of addition to an unsymmetrical double bond.

One effective initiator is Casey and Burkhardt's (diphenylcarbene)pentacarbonyltungsten (1) [2], which induces a variety of cycloalkenes to give



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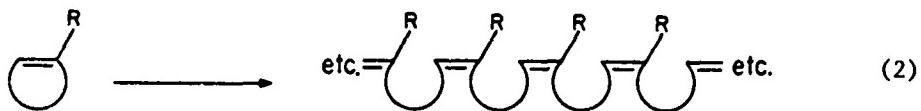
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polyalkenamers (Eq 1) [3]. The reactions, it turns out, exhibit remarkable stereoselectivity. Thus cycloheptene, for example, gives polyheptenamer



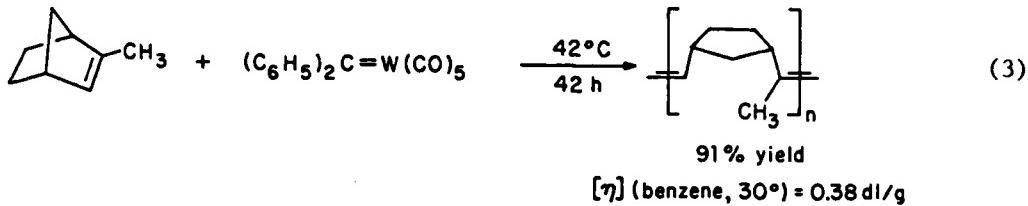
in which the double bonds are $\geq 98\%$ cis, and similar selectivity is shown by a variety of other cycloalkenes [3]. (The polymers, incidentally, are fairly large, that from cycloheptene having a weight-average molecular weight, M_w , of 1.4×10^6 and number-average molecular weight, M_n , of 2.1×10^5 .)

This metal-carbene also induces the polymerizations of a few cyclic trisubstituted olefins, and these reactions are also interestingly selective, giving polymers that are translationally invariant (Eq 2) [3e,f]. Thus the

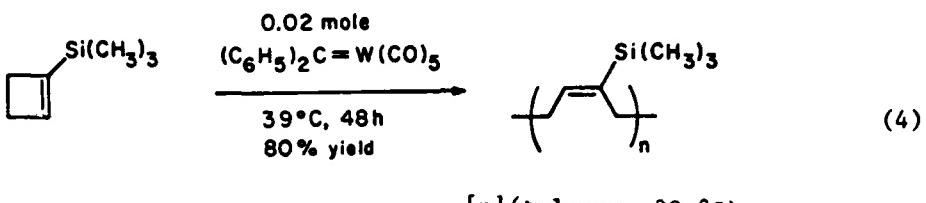


polymer from 1-methylcyclobutene is largely translationally invariant, yet not perfectly so [3e], but that from 1-methyl-trans-cyclooctene is essentially perfect (within the ca. 2% detection limits of the ^{13}C NMR method of analysis and disregarding isomerism about the double bonds) [3f]. Incidentally, the reason these experiments were done with olefins whose double bonds are strained by distortion is that unstrained trisubstituted olefins are unreactive, 1-methyl-cis-cyclooctene, for example, failing to polymerize. Another olefin with which such experiments were done is 2-methylnorbornene (Eq 3), and this olefin too with (diphenylcarbene)pentacarbonyltungsten gives the corresponding polyalkenamer in high yield (91%) and with the expected selectivity [4]. This selectivity is indicated by the absence in the polymer's

^{13}C NMR spectrum (Fig. 1) of peaks at the position indicated by the arrow, where polynorbornenamers absorb. The spectrum is labelled to show that units are present with both E- and Z-geometries about the double bonds. There is also an interesting multitude of peaks in the olefin region that may be a consequence of this variety of double bond geometries or possibly of units present having different tacticities [5]. The distinction could be made if only one enantiomer of 2-methylnorbornene were polymerized and analyzed, but the experiment remains to be done.

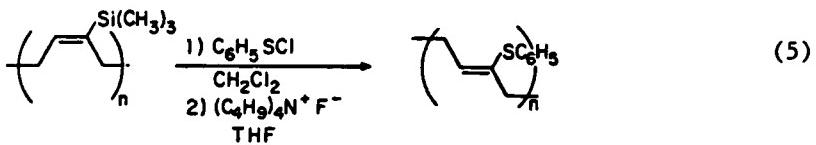


Yet another cyclic trisubstituted olefin that has given a translationally invariant polymer is 1-trimethylsilylcyclobutene (Eq 4), and in this case the polymer appears to be not only perfect (within the instrument's detection limits) in the sense that the head of one unit is always attached to the tail of the next, but also in the sense that the geometry at the point of fusion is always the same [6]. Fig. 2 shows this. It displays the ^{13}C NMR spectrum of the polymer and marks positions where peaks characteristic of units with head-to-head, with tail-to-tail, and with alternative double bond geometries might have (but did not) absorb. The spectrum shows this to be the most perfectly translationally invariant polymer ever made by metathesis! The polymer is interesting for yet another reason. It provides a basis for making functionalized olefins by metathesis. The idea is that since functional



$$[\eta] \text{ (toluene, } 30^\circ\text{C)} = \\ 2.13 \text{ dL/g}$$

groups appear to interfere with metatheses by coordinating to metals and since vinyltrimethylsilanes can be converted easily into a variety of functionalized olefins [7], the trimethylsilyl groups can serve as a surrogate for a functional group before a metathesis and then serve to introduce it afterwards. Eq 5 summarizes an experiment in which this kind of transformation appears to have been effected, for the ^1H NMR spectrum of the resulting polymer seems appropriate.

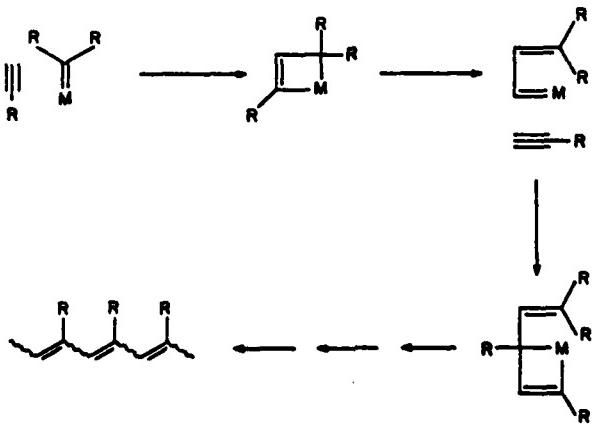


It is unfortunate that all the reactions initiated by (diphenylcarbene)pentacarbonyltungsten are not also induced by (phenylmethoxycarbene)pentacarbonyltungsten (2), the archetypical metal-carbene of E. O. Fischer, for it is much less difficult to make [8]. But that metal-carbene appears too unreactive to induce metatheses of many olefins, cyclopentene for example, although it does work with those that are strained [3b]. The two original examples are norbornene and cyclobutene [3b], but 1-trimethylsilylcyclobutene's polymerization is also induced by it [6]. (Phenylmethoxycarbene)pentacarbonyltungsten is not the

only heteroatom-stabilized (Fischer-type) metal-carbene with the ability to induce metatheses of strained olefins, a variety of related molecules having proven effective for the polymerization of norbornene [4]. Cis-(phenylmethoxy-carbene)triphenylphosphinetetracarbonyltungsten, for example, is so active that when combined at 50 °C for 51 h with 1 1/4 million times as many moles of norbornene, it gives a 21% yield of polynorbornenamer, $[\eta]$ (benzene, 30°) = 3.52 dL/g, with 75% of its double bonds cis.

(Phenylmethoxycarbene)pentacarbonyltungsten initiates the reaction of cyclobutene, but not cyclopentene, and it seems likely that if the ring were shrunk further, cyclopropenes would also prove reactive. The experiments have not been tried. However, they have been for molecules that were shrunk in size once again, for analogy suggests that two-membered rings should also give the corresponding polyalkenamers, and substituted two-membered rings should give those that are translationally invariant. In short, metal-carbenes should induce acetylenes to polymerize, and Scheme 1 depicts the essentials

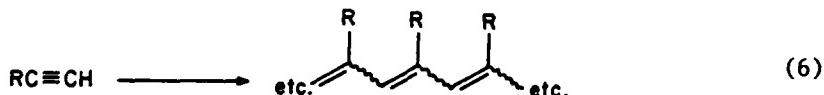
Scheme 1



of the transformation. Now metal initiators are known to induce acetylene polymerizations, but the mechanism is not usually thought to involve the steps in Scheme 1 [9]. Moreover, although there are a variety of metal-containing combinations that have been discovered to act as initiators, metal-carbenes

are not among those reported.

Accordingly, experiments were tried to see whether metal-carbenes would induce acetylenes to polymerize, and indeed 1 does [10]. 1-Hexyne, for example, after 19 h at 40 °C with 0.02 moles of 1 gives, after precipitation by methanol from a methylene chloride solution, a 60% yield of poly(1-hexyne) (Eq 6, with R = n-butyl). The polymer's intrinsic viscosity in toluene at



30 °C is 0.4 dL/g, and its molecular weights according to gel permeation chromatographic (GPC) analysis (reported in quotes as the weights of polystyrenes whose GPC analyses would be similar) are " \bar{M}_w " = 78,000, " \bar{M}_n " = 25,000. Other acetylenes, like phenylacetylene, propyne, and t-butylacetylene, also give the analogous polymers.

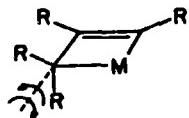
It is significant that 1 acts as an initiator for acetylene polymerization and extraordinary that even the much more available Fischer carbene 2 works [10]. Thus t-butylacetylene, for example, after 20 h at 60 °C with 0.01 moles of 2 gives, after precipitation from chloroform by methanol, a 28% yield of poly(t-butylacetylene), $[\eta]$ (heptane, 30 °C) = 1.1 dL/g, " \bar{M}_w " = 570,000, " \bar{M}_n " = 260,000. And other monosubstituted acetylenes similarly give the analogous materials. There is no doubt about the structures of the polymers, for these are shown by their magnetic resonance and infrared spectra, the ^1H and ^{13}C NMR spectra of poly(t-butylacetylene), displayed in Figs. 3 and 4, for example, exhibiting expected peaks and none that are extraneous.

The reactions also work with disubstituted acetylenes, like 2-butyne, and with mixtures of disubstituted and monosubstituted acetylenes, four parts of 4-octyne and one of phenylacetylene, for example, giving a 1 : 1 soluble copolymer with " \bar{M}_w " = 160,000, " \bar{M}_n " = 50,000.

These experiments suggest that Scheme 1 may in fact be the mechanism by which acetylenes polymerize although they do not prove this. The mechanism has other virtues as well, among which are analogy to reactions like Eq 7 from Dötz's work [11] and a felicitous account of how the stereochemistries of acetylene polymerizations vary. (These might be determined by the direction of rotation summarized in structure 3.)



However, other experiments have to be done if the route in Scheme 1 is to be proven, and one set that supports the scheme and that has



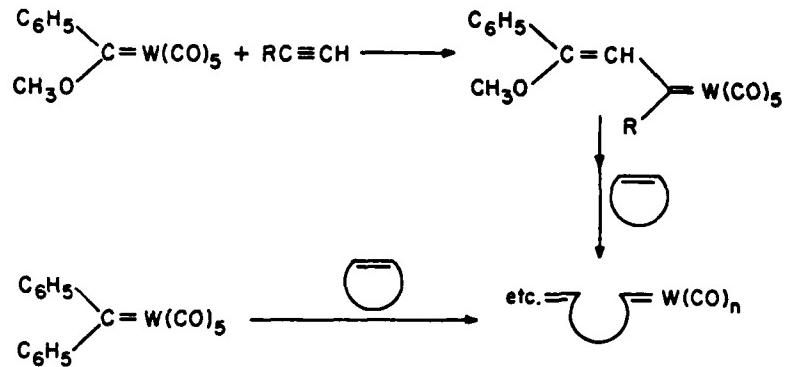
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relevance to the olefin metathesis reaction involves attempts to use acetylenes as cocatalysts for olefin metatheses [12]. The idea is that if metal-carbenes propagate both the polymerizations of acetylenes and the metatheses of olefins, then an initiator for the one reaction that fails with the other might be induced to work by the effective substrate.

The obvious experiment suggested by the research described above is to see whether an acetylene would induce the Fischer metal-carbene, 2, to initiate the polymerization of cyclopentene, and indeed it does. Thus, whereas 0.01 mole of 2 after 16 days at 50 °C shows no sign of being able to polymerize cyclopentene to polypentenamer, 0.005 moles of 2 combined with 0.05 moles of phenylacetylene is in fact effective. It gives, after 22 h at 50 °C, a 41% yield of polypentenamer that is 68% cis and has $\bar{M}_w = 188,000$ and $\bar{M}_n = 92,000$. Other acetylenes, like propyne, can be substituted for the phenyl-acetylene, but similar experiments with other olefins have been only partially successful. Cis-2-pentene, for example, fails to metathesize, and cycloheptene and cyclooctene react only very slowly. Thus the combination of cycloheptene, phenylacetylene, and 2 in the mole ratio 100 : 2 : 1 after one week at 50 °C gave, in 19% yield, polyheptenamer, $\bar{M}_w = 378,000$, $\bar{M}_n = 205,000$, but while the polymerization took a long time and the yield was low, without phenylacetylene the polymerization was not detectable. What is most remarkable, both about this polyheptenamer and about the analogous polyoctenamer (which formed even more slowly), is that the double bonds are essentially all cis. For polyheptenamer the figure is ≥98%, as evidenced by the ^{13}C NMR spectrum in Fig. 5, in which the characteristic resonance of the allylic trans-methylene is absent. This seems a noteworthy result, for the only other initiator giving this high stereoselectivity is 1 [3a], and yet the result should be anticipated if the propagating species formed according to the two paths in Scheme 2, for they would be the same whether the initiator were 1 or were 2 plus an acetylene.

The experiments described above provide syntheses for a number of polymers where in some cases other preparations have failed or given low yields, impure products, or low stereoselectivity. They also forge an interesting

Scheme 2



link between olefin metathesis and acetylene polymerization, and suggest a variety of other experiments that ultimately should test the strength of that bond.

Acknowledgements

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Figure Captions

Figure 1. ^{13}C NMR spectrum of poly(2-methylnorbornenamer) in CDCl_3 . The spectrometer frequency was 25 MHz, pulses were repeated every 1.8 s, and 3200 spectra were accumulated. The arrow points to the region where trans- and cis-polynorbornenamer have their olefin resonances, at 133.1 and 134.1 ppm.

Figure 2. ^{13}C NMR spectrum of poly-1-trimethylsilylbutenamer in CDCl_3 . The spectrometer frequency was 20 MHz, and 2600 spectra were accumulated using ca. 45° pulses repeated at 0.82 s intervals (no relaxation delay). Arrows point to where significant resonances might have appeared had there been appreciable numbers of units present with alternative stereochemistries.

Figure 3. ^1H NMR spectrum of poly(t-butylacetylene) in CDCl_3 . The spectrum is that acquired as a single scan at 90 MHz on a continuous wave spectrometer. The internal standard is tetramethylsilane. Chemical shifts are listed below the peaks and intensities above.

Figure 4. ^{13}C NMR spectrum of poly(t-butylacetylene) in CDCl_3 . The initiator for the polymerization was 2. The spectrometer frequency was 20 MHz and 5000 spectra were accumulated.

Figure 5. ^{13}C NMR spectrum of polyheptenamer made from cycloheptene, phenyl-acetylene, and 2 (molar ratios: 100, 2, 1). The solvent was CDCl_3 . Note the absence of the resonance characteristic of the allylic methylene in the trans structure.

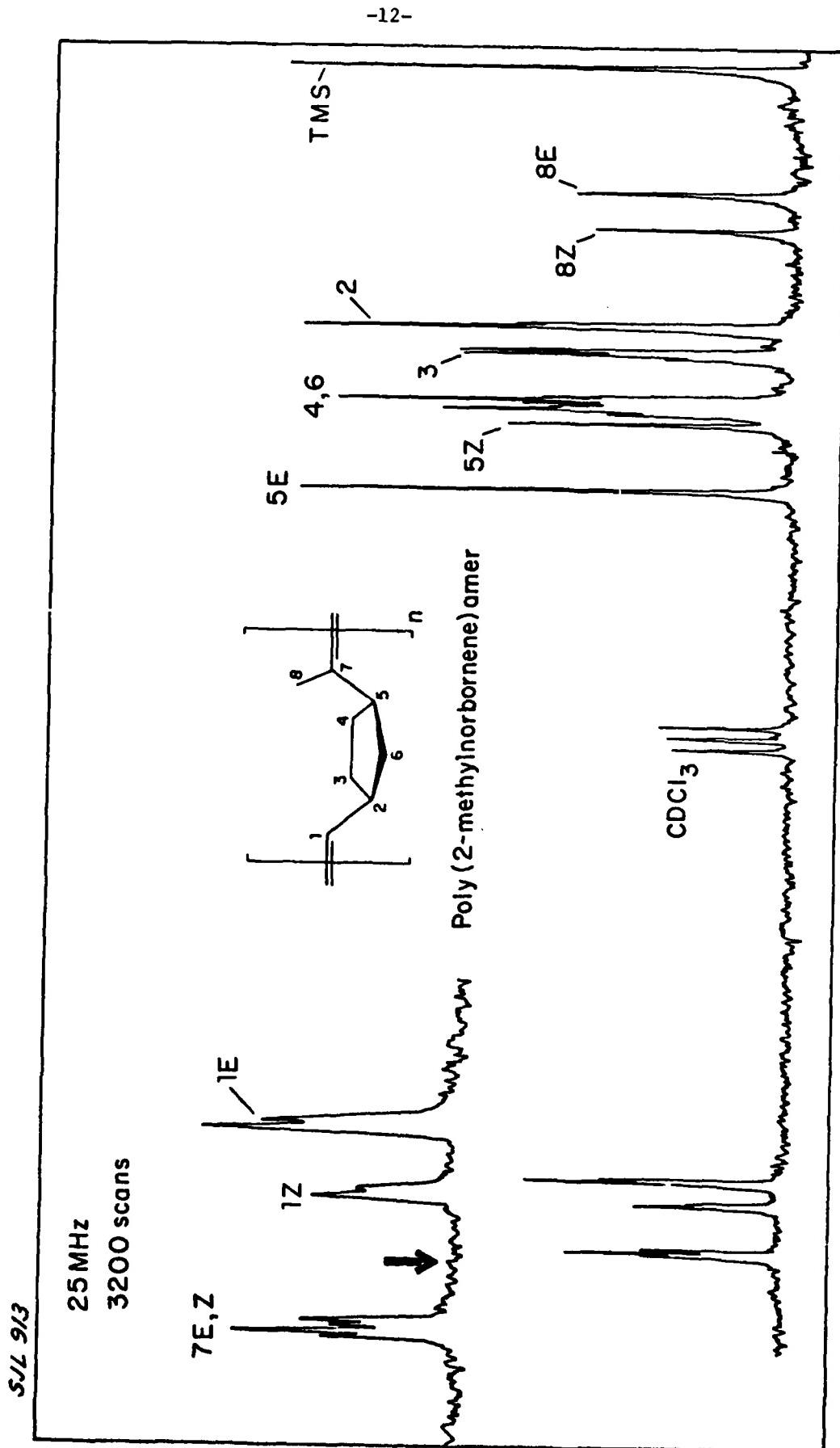
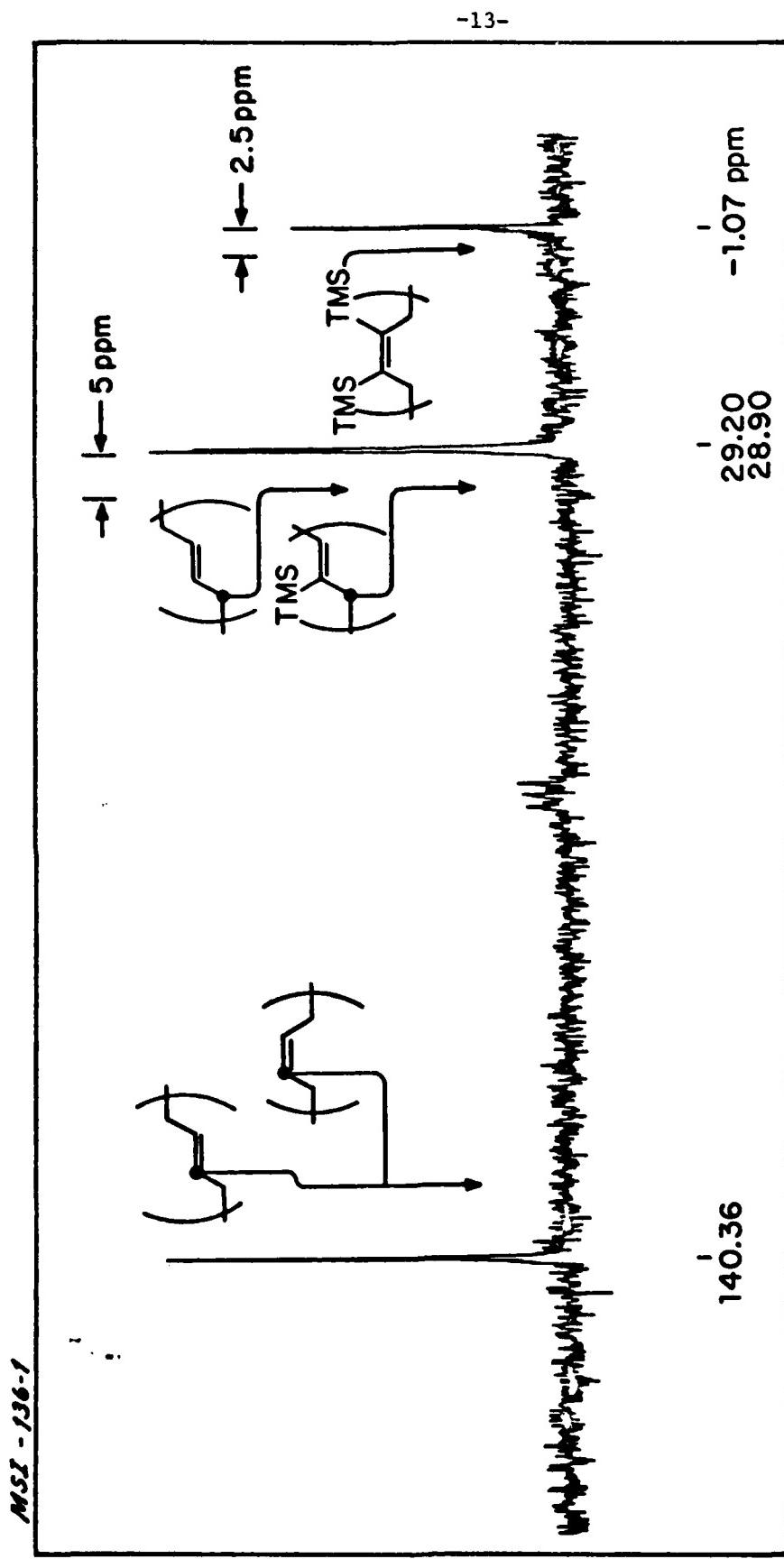
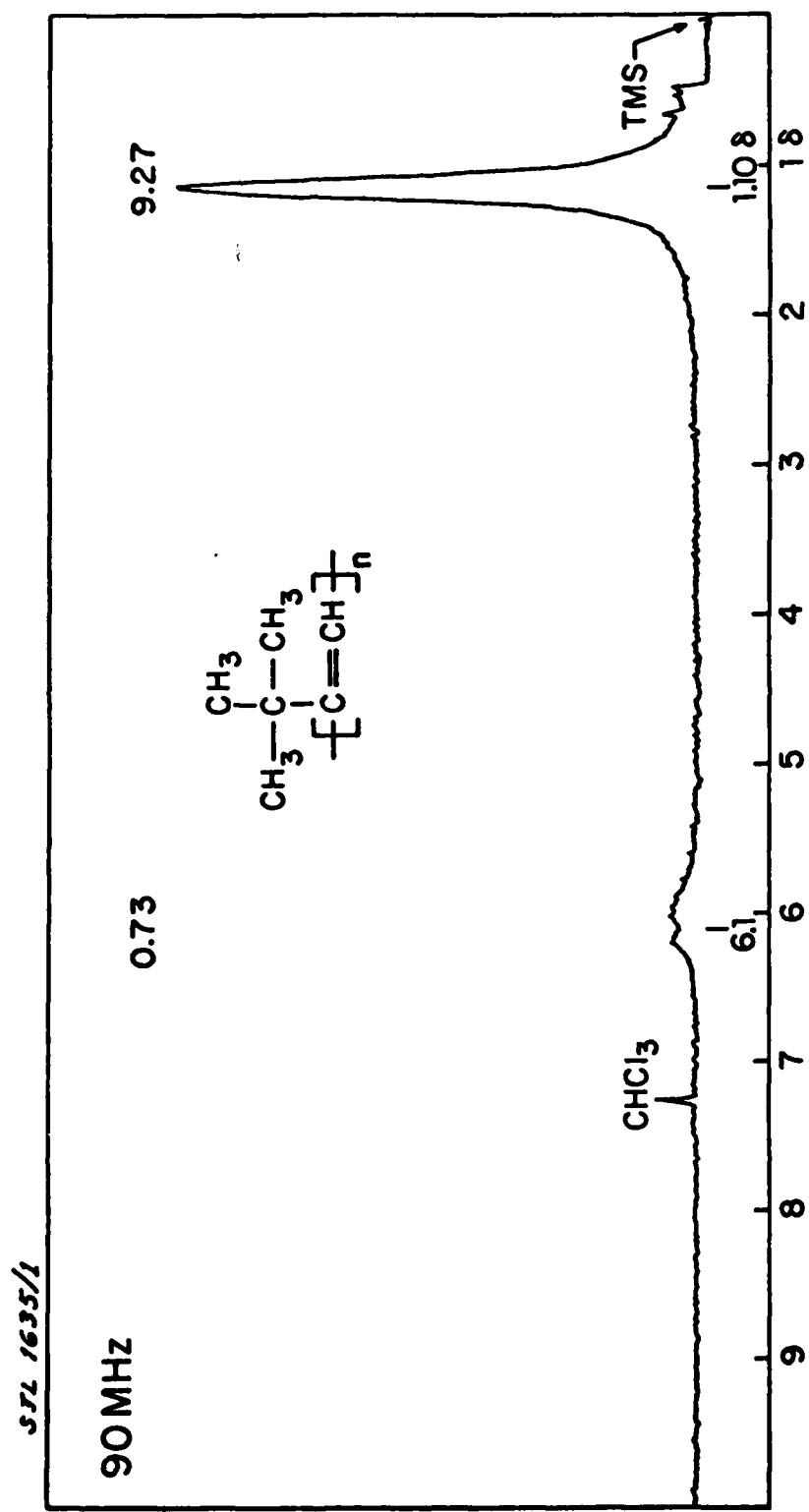
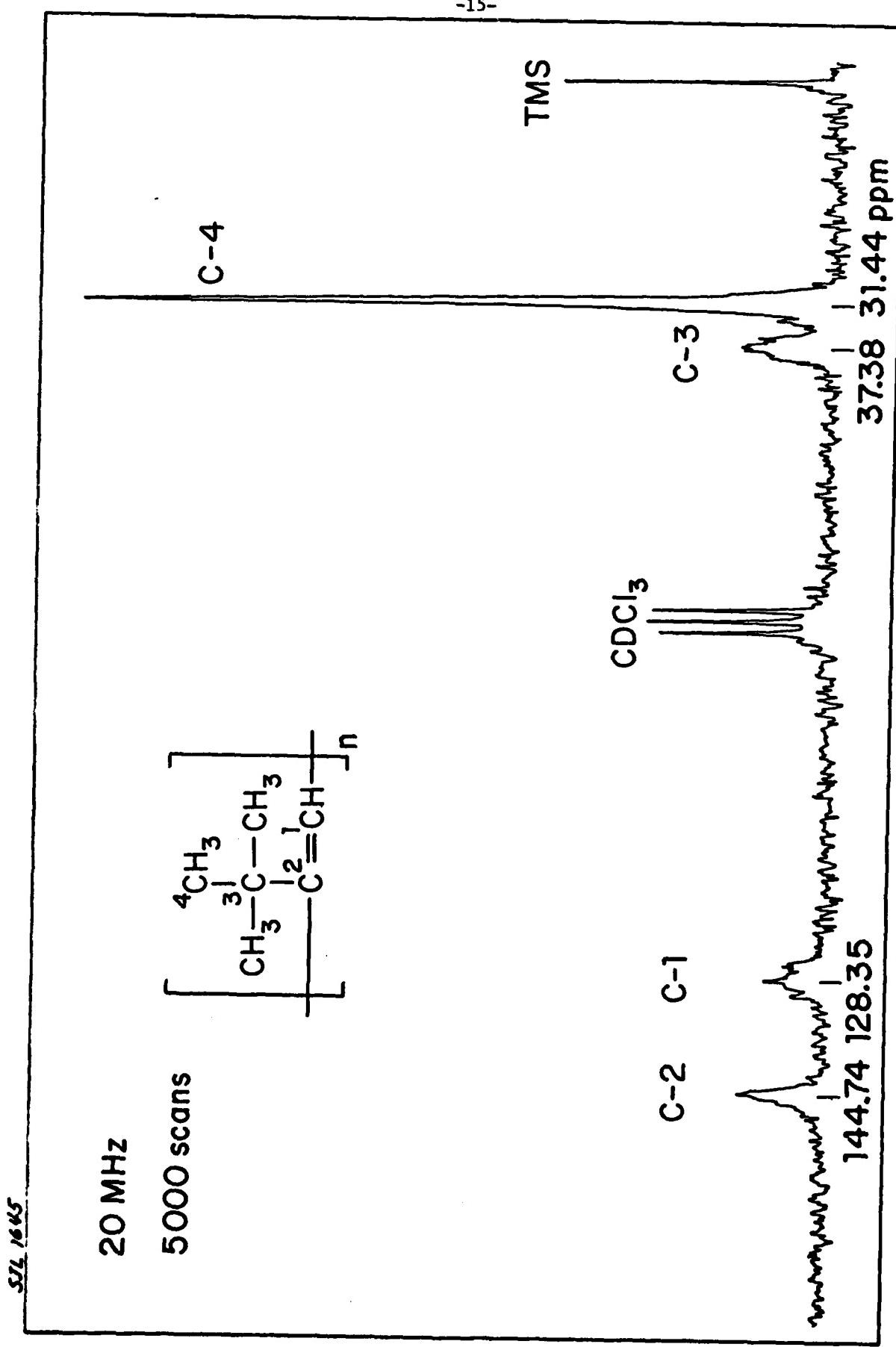
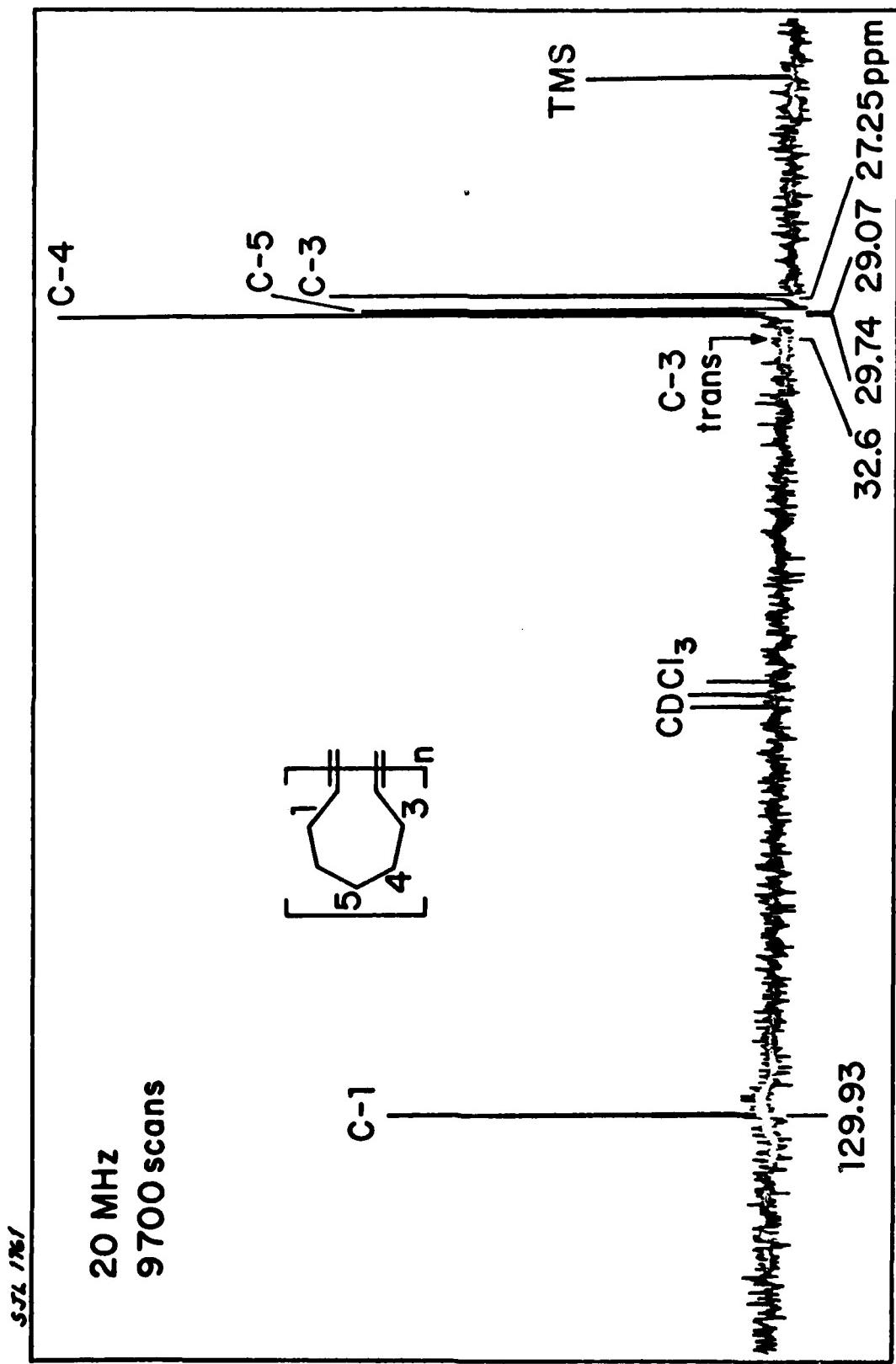


fig. 2









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